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(54) Title: METHOD OF MAKING COMPOSITE POWDER AND A COMPOSITE COATING OF A SUBSTRATE

(57) Abstract: A composite powder and a method of producing said powder, which powder comprises metal ceramic composite that consists of 25-75 per cent by volume of NiCr and of a hard phase, said hard phase being Cr_2O_3. A composite coating, especially intended for piston rings, which coating comprises metal ceramic composite consisting of 25-75 per cent by volume of NiCr and of a hard phase of Cr_2O_3. A piston ring which is coated with said composite coating.

METHOD OF MAKING COMPOSITE POWDER AND A COMPOSITE COATING OF A SUBSTRATE

Field of the Invention

The present invention relates to a method of making a composite powder. In addition, the invention relates to a composite coating for coating of a substratum, especially piston rings.

Background Art

It is already known to cover objects which are exposed to great strain in the form of friction, heating, corrosive environmental conditions etc. with different types of surface coatings which are usually resistant to abrasion and other kind of wear and tear. In certain cases, as for example in the case of piston rings for diesel engines, a problem, however, arises in that the ring coating has to be abrasion-resistant but at the same time not so hard that it damages the cylinder liner in the cylinder, in which the piston ring runs. Piston rings used in a diesel engine, for example, are exposed to extremely great strain in the form of, inter alia, high temperatures, highly corrosive environmental conditions, tensions in the piston-ring material and friction against the cylinder liner. At the same time, very high demands are made on operational reliability when such rings are used in marine engines.

In prior-art technique, for example, electrolytically applied hard chromium or ceramic chromium are used in order to increase the resistance of the coating to, for example, abrasion and corrosion. Electrolytic application of one or more layers of a material having suitable protective properties is one way of trying to increase the resistance. The problem is to produce a layer which is resistant to abrasion, corrosion and high thermal stress. Attempts to apply a plurality of layers having individually different properties to provide resis-

tance to different types of wear and tear thus are made more and more with varying success.

Another way of providing a resistant coating material is to use a composite material for forming a coating having the desired properties. For example US-3,914,507 discloses a method of producing a large number of different composite powders. By means of the method in the above-mentioned patent document, a composite powder is produced by sintering an existing powder which has a core of, for instance, kieselguhr, chromium oxide or calcium fluoride, and a coating of nickel, with another powder of, for example, chromium, which forms an alloy with the existing nickel coating with the aid of heat. A process which according to the above-mentioned document takes about 40-50 hours is, of course, highly disadvantageous. In addition, the method of sintering limits the possibilities of obtaining an alloy between nickel and chromium, a great part of the nickel and chromium remaining as separate phases also after sintering. One consequence of this incomplete alloying process is that the thermal stability of a powder-based coating of the powder material in question fails to be optimal.

Normally, thermal spraying of a mixture of powder is used in order to provide a substratum with a coating. This method gives a composite coating structure that comprises continuous zones of a substance that are more extensive than desirable. This also causes great problems of adhesion of the particles in the powder that are to form the coating. The poorer adhesion due to the continuous zones gives rise to indications of cracking , which decreases the strength of the coating. Also the thermal stability is affected in a negative manner.

JP10088312 discloses a HVOF-sprayed coating for piston rings, the coating comprising a first nickel group (60-90 per cent by weight) which contains Cr and Mo, and a second group (10-40 per cent by weight) which comprises Cr_2O_3 or MoO_3 and is doped with SiO_2. Mo is used in prior-

art technique in order to cause adhesion between the remaining parts of the coating. In this type of applications, i.e. piston rings, Mo has the disadvantage of giving coatings electrochemically, unstable properties. In addition, Mo has low resistance to oxidation, which means that it is thermally unstable in this type of applications. SiO_2 is used in prior-art technique to establish mechanical bonding between the remaining parts of the coating, but has the disadvantage of developing brittleness in this type of applications.

A solution thus still has to be found to the problem of providing a composite coating that is intended for covering a substratum and that exhibits thermal stability during production as well as use while at the same time possessing a high degree of resistance to wear and corrosion.

Summary of the Invention

The disadvantages mentioned in the background given above are initially eliminated by providing a homogeneous composite coating which is disclosed in the independent claim 1. The substratum covered with the composite coating preferably consists of a piston ring in accordance with claim 3. The composite coating is formed by a composite powder which is produced by means of a method according to claim 5. Said composite powder is applied to the substratum as a coating. Preferred embodiments as well as a method according to the invention will appear from the dependent claims.

In preparation to being applied to the substratum, the particles of the composite powder are sifted in order to separate out the desired size fraction of the composite powder for applying the coating. Depending on what method is used to cover the substratum, a certain amount of the particles is lost or is transformed in the application process, for which reason the concentrations of the phases in the coating can differ compared with the

originally included concentrations of the phases for producing the composite powder.

Consequently, the invention relates to a composite coating, which is especially intended for piston rings and which comprises a metal ceramic composite, and it is characterised in that the metal ceramic composite consists of 25-75 per cent by volume of NiCr and a hard phase, said hard phase being Cr_2O_3. Thus, the coating according to the invention consists of a metallic phase and a hard phase or metal ceramic phase. From a mechanical and tribological point of view, the coating offers an optimal combination of the properties of the materials included. The finished coating has a corrosion resistance which is equivalent to that of a coating of hard chromium. By combining NiCr with a hard phase from the above-mentioned group, a coating is, however, obtained that possesses considerably better thermal properties than, for instance, hard chromium, which is a common wearing layer on piston rings, a feature which makes the coating according to the invention especially suitable for covering said piston rings. The combination of a ductile phase and a hard phase in the coating results in a very high resistance to abrasion and at the same time it provides a certain ductility. This ductility of the coating is a great advantage, for instance, when it is used to coat piston rings.

In a preferred embodiment of the coating according to the invention, the hard phase of the composite coating consists of Cr_2O_3. The chromium oxide has very satisfactory tribological properties. Another advantage of a coating of precisely NiCr and Cr_2O_3 is that a strong metallurgical bond is established between the chromium in the metallic phase and that of the oxide phase.

In a preferred embodiment of the invention, the composite coating has a porosity of 2-10 per cent by volume. The porosity of the coating imparts to the cavities in the coating a certain capacity of absorbing deformations

arising in the material and therefore to a certain extent the formation of cracks in the coating is prevented. This coating therefore is regarded as more ductile and the phenomenon is referred to as false ductility. A further advantage of the presence of pores is that they can function as lubricating-oil buffers.

The composite coating can be applied to a substratum in different ways in accordance with prior-art techniques. Examples of known techniques of covering a substratum with a coating is by means of laser or other welding methods, plasma jet spraying, and HVOF method, methods which will not be described in more detail herein.

The invention also relates to a piston ring, which is provided with a coating that comprises a metal ceramic composite and which is characterised in that the metal ceramic composite consists of 25-75 per cent by volume of NiCr and a hard phase, said hard phase being Cr_2O_3. The proportion of pores in the piston-ring coating amounts to 2-10 per cent by volume.

The invention also relates to a method of producing a composite powder, characterised by preparing an aqueous suspension consisting of a mixture of 25-75 per cent by volume of NiCr and a hard phase, said hard phase being Cr_2O_3, obtaining particles from said suspension and processing said particles by means of a drying method in order to form the composite powder.

One advantage of the above-mentioned method is that thanks to the composite powder produced thereby it becomes possible to obtain a powder, which, after having been applied as a composite coating to a substratum, forms a composite coating that not only possesses satisfactory thermal resistance and corrosion resistance but also a high wearing strength. The subsequent application of the composite powder to the substratum, wherein a coating having all the three desired properties is formed, is, of course, facilitated when it can be

achieved by one single material. Moreover, the method according to the invention allows the powder to be formed from a stable suspension in such a way that homogeneous and satisfactory particles, or so-called granules, are formed.

The inventive idea concerns a method according to which the particles are obtained from the suspension by allowing the suspension to drip into a refrigerant, whereby cooled particles are formed. This method will in the following be referred to as freeze granulation. This freeze granulation is achieved, for example, by spraying the suspension as formed directly into liquid nitrogen, the sprayed droplets instantaneously forming frozen spherical particles. In accordance with the inventive method, the drying method with a view to forming the composite powder from the particles comprises freeze-drying. Freeze granulation of the powder material has a large number of advantages over conventional methods, of which the following advantages deserve to be mentioned.

The frozen droplets produced in the process of freeze granulation have the same composition as the original suspension. Thus, migration of fine particles and possibly of binders during the drying, which is a problem in alternative methods of drying, such as evaporation, is avoided. The migration gives rise to inhomogeneous granulates. A very high yield of material in the process is another advantage gained by the method of freeze granulation. In addition, the density of particles can be controlled by means of the dry contents (the amount of powder) in the suspension.

According to yet another aspect of the method, the method of producing a composite powder of NiCr and the hard phase comprises spray drying. The method involving spray drying of the particles is a further alternative of producing the powder. The above-mentioned methods of production should only be regarded as examples of preferred methods of producing the composite powder and should not

be considered to limit the inventive idea, but also other methods of producing the composite powder according to the invention are possible.

The invention also relates to a method of producing said composite powder according to which a dispersing agent in the form of a charged polymer is added to the suspension. In order to give the particles as satisfactory properties as possible, it is important that the product on which the process is based is homogeneous and well dispersed. One example of a negatively charged polymer which is suitable as a dispersing agent is polyacrylic acid. The advantage of using a polymer as a dispersing agent in the production of the powder in question is that it is removed from the material by heat conduction when the layer is applied on the substratum as a coating.

The invention also relates to a method of producing said composite powder, according to which a binder is added to the suspension. The choice of binder is made with a view to making the particles as strong as possible. One example of a binder is polyvinyl alcohol (PVA). In order to ensure that the binder does not become too hard and brittle while the powder is drying, different plasticizers or softeners can be added. Polyethylene glycol (PEG) is one example of a softener. A further advantage of using the above-mentioned softeners in the production of the powder in question is that they are removed from the material by heat conduction, for example, when the layer is applied to the substratum as a coating.

In order to prevent the chromium oxide from forming continuous zones in the coating, in which zones cracks can arise and grow due to low ductility, the dried particles may be pre-sintered at a temperature of 1000-1500°C for 30-90 minutes. These zones may arise partly due to the fact that the composite particles disintegrate during the very spraying process. The method of pre-sintering the dried particles at a temperature of 1000-1500°C for

30-90 minutes improves the inner strength of the composite powder, which is one way of decreasing the risk of disintegration when the composite powder is applied in the form of a coating.

Description of a Preferred Embodiment

A preferred embodiment of the method according to the invention and products produced by means of the method according to the invention will be described in the following. The described embodiment should not be regarded as limiting but is given by way of example only.

As a starting point when producing a composite powder according to an inventive method, it is convenient to use an aqueous suspension. Expressed in simple terms, a preferred method comprises the following steps. A powder mixture containing 60 per cent by volume of NiCr and 40 per cent by volume of Cr_2O_3 is added to the aqueous suspension. In this case, NiCr serves to produce an alloy comprising about 80 per cent by weight of Ni and about 20 per cent by weight of Cr. Dispersing agents are added to the aqueous suspension, which is thereafter stirred to ensure that a homogeneous suspension is obtained. Binders are added. In a preferred embodiment, softeners are added. The resulting suspension is mixed additionally. According to a preferred method of the invention, the suspension is subsequently freeze-sprayed and freeze-dried, causing particles to form. In order to achieve an optimum result when covering a substratum with the resulting composite powder, the powder is sifted in such a manner that a suitable size fraction of the powder is obtained. This size fraction is preferably 40-100 µm. Particles larger than 150 µm cannot be used in plasma-jet spraying using today's methods.

The invention will now be described in more detail by means of a preferred embodiment which relates to a method of producing said composite powder according to which a dispersing agent in the form of a charged polymer

is added to the suspension. In order to give the particles as satisfactory properties as possible, it is important that the product on which the process is based is homogeneous and well dispersed. One example of a negatively charged polymer that is suitable as a dispersing agent is polyacrylic acid. The advantage of using a polymer as a dispersing agent in the production of the powder in question is that it is removed from the material by heat conduction when the layer is applied to the substratum as a coating. The amount of dispersing agent has to be adapted to ensure production of as many particles as possible within the range of 45-95 µm, which is the optimal size for plasma-jet spraying.

In a preferred embodiment which relates to a method of producing said composite powder, according to which a binder is added to the suspension. The choice of binder is made with a view to making the particles as strong as possible. One example of a binder is polyvinyl alcohol (PVA). In order to ensure that the binder does not become too hard and brittle while the powder is drying, a softener is added. Polyethylene glycol (PEG) is one example of a softener.

The inventive idea concerns a method according to which particles are formed from the suspension by allowing the suspension to drip into a refrigerant, whereby cooled particles are formed. This method, known as freeze granulation, also comprises subsequent freeze-drying, in which process the water content in the frozen granules is sublimed. This freeze granulation is achieved, for example, by spraying the suspension as formed directly into liquid nitrogen, whereby frozen spherical particles form instantaneously.

The composite powder according to the invention, consists of 25-75 per cent by volume of NiCr before sifting, but more preferably of 50-70 per cent by volume of NiCr, and most preferably of about 60 per cent by volume of NiCr. The remaining amount of the composite powder

consists of a hard phase as a supplement to the first amount of NiCr, the hard phase being Cr_2O_3.

In order to coat a substratum with the composite material according to the invention, a prior-art method such as a HVOF method, laser, welding or plasma-jet spraying methods are suitably used. In the coating process, the composite powder is affected by very high temperatures, which can change the chemical composition somewhat.

The piston ring may be preheated and/or post-heated in a conventional manner in a conventional oven, before and after the coating method is carried out.

After sifting the composite powder and applying it to a substratum, a coating according to the invention is obtained. The distribution in the coating suitably is 2-10 per cent by volume of pores, but more preferably 3-8 per cent by volume of pores and most preferably 4-7 per cent by volume of pores. The amount of NiCr suitably is between 25 and 75 per cent by volume, but more preferably between 30 and 55 per cent by volume and most preferably between 35 and 45 per cent by volume. The essentially remaining part of the coating, which contains other matter than pores and NiCr, consists of the hard phase.

A composite coating according to a preferred embodiment of the invention, which comprises NiCr and chromium oxide has been found to have a resistance to dry wear equivalent to or superior to that of hard chromium. In one embodiment, the thickness of the coating is between 0.1 and 1.2 mm, however, more preferably between 0.5 and 1.0 mm and most preferably between 0.7 and 0.8 mm. The capacity of adhesion to the substratum has been found to be equal to or surpass that of hard chromium, as also its passivity in a strongly corrosive environment. The porosity of the coating is 2-10 %. All the properties stated above show that the coating is eminently adapted to cover piston rings. Hardness testing according to the Rockwell hardness test shows that the hardness of the coating is

about 65 HR 62.5 kg. After heat treatment at 500°C for 24 hours, the coating surprisingly enough shows an increase of hardness to about 70 HR 62.5 kg.

In this application, powder materials, should be regarded to include not only conventional powder materials but also such powder materials that have been mixed with a binder in order to produce a creamy consistency, which may be an advantage when applying the powder material to the piston-ring blank.

By means of the method according to the invention, a coating of metal ceramic chromium is provided, the properties of which are equivalent to or superior to those of the coatings which are available today. It will also be understood that the above-described features can be combined in different ways in order to provide further varieties within the scope of the invention. The method according to the invention and the products produced thereby thus are not limited to that described above. For instance, the application of the substratum can be carried out in several ways. The choice of dispersing agents, binders and softeners can also be varied without deviating from the idea of the invention. The invention can thus be further modified in a number of ways within the scope of the inventive idea and as defined in the appended claims.

CLAIMS

1. A composite coating, especially intended for piston rings, which coating comprises metal ceramic composite, c h a r a c t e r i s e d in that the metal ceramic composite consists of 25-75 per cent by volume of NiCr and of a hard phase, said hard phase being Cr_2O_3.

2. A composite coating as claimed in claim 1, which coating has a porosity of 2-10 per cent by volume.

3. A piston ring, which is provided with a coating comprising a ceramic metal composite, c h a r a c t e r i s e d in that the metal ceramic composite consists of 25-75 per cent by volume of NiCr and of a hard phase, said hard phase being Cr_2O_3.

4. A piston ring as claimed in claim 3?, which has a coating with a porosity of 2-10 per cent by volume.

5. A method of producing composite powder, c h a r a c t e r i s e d by preparing an aqueous suspension consisting of a mixture of 25-75 per cent by volume of NiCr and a hard phase, said hard phase being Cr_2O_3, obtaining particles from said suspension by allowing the suspension to drip into a refrigerant, whereby cooled particles are formed and processing said particles by means of a drying method in order to form the composite powder.

6. A method as claimed in claim 5, wherein the drying method to form the composite powder from the particles comprises freeze-drying.

7. A method as claimed in any one of claims 5-6, in which a dispersing agent in the form of a charged polymer is added to the suspension.

8. A method as claimed in any one of claims 5-7, in which a binder is added to the suspension.

9. A method as claimed in any one of claims 5-8, in which a softener is added to the suspension.

10. A method as claimed in any one of claims 5-9, in which the dried particles are pre-sintered at a temperature of 1000-1500°C for 30-90 minutes.

11. A composite powder characterised in that it is produced according to a method as claimed in any one of claims 5-10.

12. A composite coating, especially intended for piston rings, which coating comprises metal ceramic composite characterised in that the composite coating is formed from a composite powder, which is produced according to a method as claimed in any one of claims 5-10.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B22F 1/00, C23C 4/04, F16J 9/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B22F, C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO INTERNAL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	File WPI, Derwent accession no. 2000-157051, NIPPON PISTON RING CO LTD: "Wear-resistant coating slide for components such as piston rings used in diesel engine - has surface layer formed on base material by plasma metal spray, which consists of predetermined amount of molybdenum, nickel, chromium alloy, aluminium oxides chrome and silicon dioxides", JP,A,2000017419, 20000118, DW200014 --	1-12
A	File WPI, Derwent accession no. 1998-267533, NIPPON PISTON RING CO LTD. et al: "Wear-resistant sprayed coating layer for piston ring of IC engine - contains first material a nickel group and second material of chromium oxide or molybdenum oxide doped with silicon d:oxide", JP,A,10088312, 19980407, DW199824 --	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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